

UDC 666:65:546.73:546.654:546.681

CRYSTAL STRUCTURE AND IR SPECTRA OF LANTHANUM COBALTITES-GALLATES

N. N. Lubinskii,¹ L. A. Bashkirov,¹ G. S. Petrov,¹ S. V. Shevchenko,¹
I. N. Kandidatova,¹ and M. V. Bushinskii¹

Translated from *Steklo i Keramika*, No. 2, pp. 17–20, February, 2009.

Cobaltites-gallates in the binary system $\text{LaCoO}_3 - \text{LaGaO}_3$ are synthesized. X-ray phase analysis showed that a continuous series of solid solutions with the composition $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ is formed in the system investigated. It is determined that solid solutions with $0 < x \leq 0.7$ and $0.7 < x \leq 1.0$ possess rhombohedrally and orthorhombically distorted perovskite structure, respectively. Analysis of the dependence of the absorption-band frequency of the IR spectra of the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ which is due to stretching vibrations on the degree of substitution of Ga^{3+} ions for Co^{3+} ions in LaCoO_3 showed that the morphotropic boundary separating the region of the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ with rhombohedrally and orthorhombically distorted perovskite structure passes near the composition of the solid solution with x slightly less than 0.7.

Cobaltites of rare-earth elements and solid solutions based on them with perovskite structure possess singular magnetic and electric properties as well as appreciable electrochemical and catalytic activity [1]. They are being intensively studied in many science centers because of the enormous scientific significance of the results and the practical applications of these materials as resistors and electrode materials for galvanic components with a solid electrolyte as well as for fabricating ceramic membranes for obtaining pure oxygen from air and devices in which the catalytic properties and membrane separation of gas mixtures are used simultaneously [2]. Solid solutions based on lanthanum gallate LaGaO_3 also have high oxygen-ionic conductivity [3, 4], and they are promising materials for fabricating ceramic membranes.

The physical-mechanical properties of lanthanum cobaltites and cobaltites of other rare-earth elements are determined to a large extent by the spin state of the $3d^6$ electrons of cobalt Co^{3+} , which at temperatures close to 0 K are predominately in a slow-spin state ($t_{2g}^6 e_g^0$), and as temperature increases they gradually transform into intermediate-spin ($t_{2g}^5 e_g^1$) and high-spin ($t_{2g}^4 e_g^2$) states [5–7]. In the perovskite structure, the radius of the Co^{3+} ions in the low-, intermediate-, and high-spin states is 0.545, 0.560, and 0.610 Å, respectively [6]. In this connection, the crystal structure of the

rare-earth cobaltites and solid solutions based on them as well as a number of the physical properties (magnetic susceptibility, electric conductivity, IR spectra) exhibit anomalous behavior as a function of temperature and composition [5–7].

The crystal structure and the magnetic, electric, and other properties of solid solutions based on lanthanum cobaltite, in which partial heterovalent substitution of alkali-earth elements for the La^{3+} ions or isovalent substitution of paramagnetic $3d$ transition elements for the Co^{3+} ions is performed, have been studied in greatest detail. The crystal structure and the electric conductivity and other properties of solid solutions based on lanthanum cobaltite which are formed with isovalent substitution of diamagnetic ion, for example, Ga^{3+} ions, for the Co^{3+} ions, have been much less studied. At room temperature lanthanum cobaltite LaCoO_3 and lanthanum gallate LaGaO_3 possess rhombohedrally ($a = 5.341$ Å, $a = 60.990^\circ$ [8]) and rhombically ($a = 5.487$, $b = 5.520$, $c = 7.752$ Å) distorted crystal structure of perovskite. Mutual dissolution of lanthanum cobaltite and gallate with formation of the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ can be expected to occur in the binary system $\text{LaCoO}_3 - \text{LaGaO}_3$.

The objective of the present work is to investigate the effect of isovalent substitution in LaCoO_3 of diamagnetic gallium ions Ga^{3+} with a completely filled $3d$ shell ($3d^{10}$) for paramagnetic ions Co^{3+} with a partially filled $3d$ shell ($3d^6$) on the crystal structure and IR spectra of the solid solutions formed $\text{LaCo}_{1-x}\text{Ga}_x\text{O}$ as promising materials for fabricating membranes and other articles for electronic technology.

¹ Belarus State Technological University, Minsk, Belarus; Science and Applications Center of the National Academy of Sciences of Belarus on Materials Science, Minsk, Belarus.

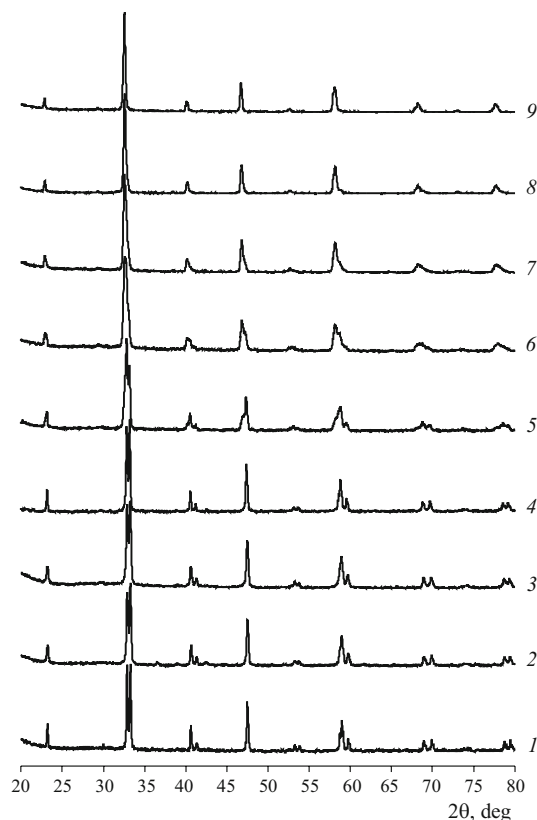


Fig. 1. X-ray diffraction patterns of samples of the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ with $x = 0$ (1), 0.10 (2), 0.20 (3), 0.30 (4), 0.50 (5), 0.70 (6), 0.80 (7), 0.90 (8), and 0.95 (9).

The cobaltites-gallates $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($x = 0, 0.15, 0.30, 0.50, 0.70, 0.80, 0.90, 0.95$, and 1.00) were obtained by the ceramic method from lanthanum oxide, cobalt oxide Co_3O_4 , and gallium. All reagents were chemically pure grade.

The powders of the initial compounds, taken in prescribed molar ratios, were mixed and ground in a Pulverizette 6 planetary mill with the addition of ethanol. The mix obtained was pressed under pressure 50–75 MPa into 25 mm in diameter and 5–7 mm high pellets and then sintered at 1250 °C in air for 4 h. After pre-sintering the pellets were pulverized, ground, and pressed into 5 × 5 mm² and 30 mm long bars, which were sintered at 1250 °C in air for 4 h.

X-ray phase analysis of the samples was performed with a D8 ADVANCE diffractometer (CuK_α radiation). The parameters of the crystal lattice were calculated using the RTP program. A NEXUS IR Fourier spectrometer (THREMO NICOLET Company) was used to record the IR spectra of the synthesized cobaltites-gallates $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ in pelleted mixtures with KBr (chemically pure) in the wavelength range 350–900 cm⁻¹.

Analysis of the x-ray diffraction patterns (Fig. 1) showed that the samples of lanthanum cobaltites-gallates were single-phase and that a continuous series of solid solutions

TABLE 1.

Value of x for $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$	d , Å (rhombohedral structure)		
	d_{220}	d_{208}	$\Delta d = d_{220} - d_{208}$
0	1.3607	1.3443	0.0164
	1.3612*	1.3444*	0.0168*
0.10	1.3607	1.3448	0.0159
0.15	1.3612	1.3448	0.0164
0.20	1.3612	1.3453	0.0159
0.25	1.3622	1.3473	0.0149
0.30	1.3633	1.3484	0.0149
0.50	1.3638	1.3499	0.0139
0.70	1.3685	1.3585	0.0099

* According to the data of [10].

TABLE 2.

Value of x for $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$	d , Å (orthorhombic structure)		
	d_{040}	d_{224}	d_{400}
0.80	1.3770	1.3738	1.3722
0.90	1.3786	1.3738	1.3706
0.95	1.3797	1.3738	1.3711
1.00	1.3798*	1.3730*	1.3717*

* According to the data of [9].

$\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ with a perovskite crystal structure is formed in the system $\text{LaCoO}_3 - \text{LaGaO}_3$. As the degree of substitution of Ga^{3+} ions for Co^{3+} ions increases a gradual transition is observed from a rhombohedrally distorted perovskite structure of LaCoO_3 (see Fig. 1, curves 1–6) to an orthorhombically distorted perovskite structure for lanthanum gallate LaGaO_3 (see Fig. 1, curves 7–9). This is seen in the x-ray diffraction patterns of $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($0 \leq x \leq 0.7$) samples, where as the degree of substitution increases a gradual transformation of two close-lying x-ray peaks is observed in the range of angles $2\theta = 33, 41, 53, 59, 69$, and 79° into a single deformed peak.

The interplanar distances d_{220} and d_{208} and their difference ($\Delta d = d_{220} - d_{208}$) for two close lying x-ray peaks (220) and (208) in the range of angles $2\theta \approx 69^\circ$ are presented in Table 1. These data show that as the degree of substitution increases from 0 to 0.7 the interplanar distances d_{220} and d_{208} gradually increase and their difference with x increasing from 0 to 0.5 gradually decreases — from 0.0164 Å for LaCoO_3 to 0.0099 Å for the solid solution with $x = 0.7$.

The solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($0.8 \leq x < 1.0$) already have the crystal structure of orthorhombically distorted perovskite. For them, the values of the interplanar distances d_{040} , d_{224} , and d_{400} calculated from the x-ray peaks (040), (224), and (400) are presented in Table 2 for angles $2\theta \approx 69^\circ$.

Of these peaks, the most intense one is the peak (224); the intensity of the peak (040) is slightly lower; and, the intensity of the peak (400) is much lower, which is in good agreement with the reference data for LaGaO_3 [9].

All this shows that in the binary system $\text{LaCoO}_3 - \text{LaGaO}_3$ the morphotropic boundary of the transition of the crystal structure of the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ from rhombohedrally into orthorhombically distorted perovskite structure lies near the solid solution composition with x slightly greater than 0.7. In the composition range of the solid solution with a rhombohedral structure the parameters a and c of the crystal lattice increase nonlinearly — from $a = 5.428 \text{ \AA}$, $c = 13.0930 \text{ \AA}$ for LaCoO_3 to $a = 5.4557 \text{ \AA}$, $c = 13.1567 \text{ \AA}$ for the solid solution $\text{LaCo}_{0.5}\text{Ga}_{0.5}\text{O}_3$. Here, it should be noted that the crystal lattice parameters obtained for LaCoO_3 in the present work are in good agreement with the values presented in [10] ($a = 5.4445 \text{ \AA}$, $c = 13.0936 \text{ \AA}$). The parameters a , b , and c for orthorhombically distorted perovskite for the solid solution $\text{LaCo}_{0.05}\text{Ga}_{0.95}\text{O}_3$ ($a = 4.4849 \text{ \AA}$, $b = 5.5168 \text{ \AA}$, $c = 7.7670 \text{ \AA}$) agree with the values of these parameters for LaGaO_3 [9].

The IR absorption spectra of the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($0 \leq x \leq 0.5$) with the crystal structure of rhombohedrally distorted perovskite in the wave number interval $670 - 520 \text{ cm}^{-1}$ have two absorption bands — ν_{s-h} and ν_{s-l} , which are due to the vibrations of the $\text{Co}(\text{Ga}) - \text{O}$ bonds (Fig. 2, curves 1 – 7). As the degree of substitution of the Ga^{3+} ions for the Co^{3+} ions increases to 0.5, the frequencies of the absorption band ν_{s-h} gradually increase from 598 cm^{-1} for LaCoO_3 (see Fig. 2, curve 1) to 630 cm^{-1} for the solid solution with $x = 0.5$ (see Fig. 2, curve 7) and the frequencies of the absorption band ν_{s-l} gradually decrease from 564 cm^{-1} for LaCoO_3 to 546 cm^{-1} for the solid solution with $x = 0.5$. As a result of such oppositely directed change of the frequencies of the absorption bands ν_{s-h} and ν_{s-l} an increase of the degree of substitution from 0 to 0.5 corresponds to a gradual substantial increase of the difference frequencies ($\Delta\nu = \nu_{s-h} - \nu_{s-l}$) from 34 cm^{-1} for LaCoO_3 to 84 cm^{-1} for the solid solution with $x = 0.5$.

The IR spectra of the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($0.70 \leq x \leq 0.95$) in the wave number range $670 - 500 \text{ cm}^{-1}$ also have two absorption bands which are due to stretching vibrations (Fig. 2, curves 8–11). However, the frequency ν_{s-l} of the absorption band of these solid solutions for $x > 0.5$ with orthorhombically distorted perovskite structure is substantially shifted in the direction of smaller values ($517 - 522 \text{ cm}^{-1}$) as compared with the frequency of a similar absorption band of solid solutions with a rhombohedrally distorted perovskite structure with $0 \leq x \leq 0.5$ ($564 - 546 \text{ cm}^{-1}$). For solid solutions with $0.70 \leq x \leq 0.95$ an increase of the degree of substitution from 0.70 to 0.95 results in a decrease of the frequencies ν_{s-h} and ν_{s-l} by 10 and 5 cm^{-1} , respectively. Their difference ($\Delta\nu = \nu_{s-h} - \nu_{s-l}$)

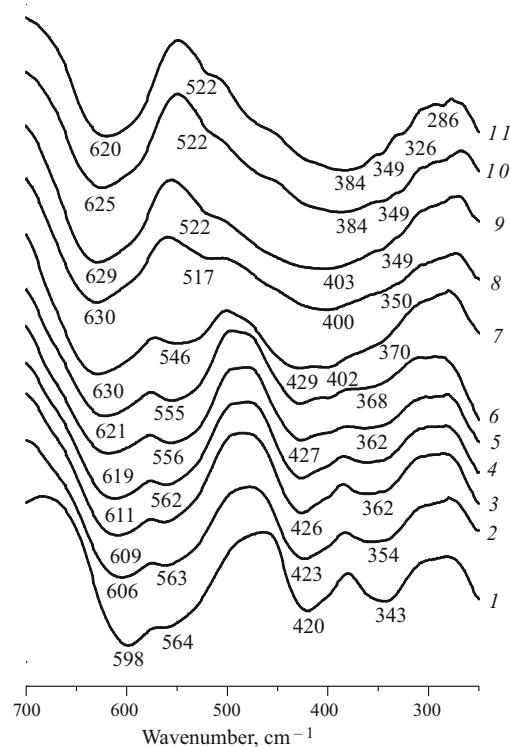


Fig. 2. IR spectra of samples of the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ with $x = 0$ (1), 0.10 (2), 0.15 (3), 0.20 (4), 0.25 (5), 0.30 (6), 0.50 (7), 0.70 (8), 0.80 (9), 0.90 (10), and 0.95 (11).

decreases from 113 cm⁻¹ for the solid solution with $x = 0.70$ to 98 cm⁻¹ for the solid solution with $x = 0.95$.

Since the frequency of the ν_{s-l} (517 cm^{-1}) of the solid solution with $x = 0.7$ (Fig. 2, curve 8) is substantially lower than the frequency ν_{s-l} (546 cm^{-1}) of the absorption band of the solid solution with $x = 0.5$ (see Fig. 2, curve 7) with a rhombohedrally distorted perovskite structure and differs only negligibly from the frequency ν_{s-l} (522 cm^{-1}) of solid solutions with an orthorhombically distorted perovskite structure for $0.80 \leq x \leq 0.95$ (see Fig. 2, curves 9 – 11), the solid solution with $x = 0.7$ probably also possesses a crystal-line structure of orthorhombically and not rhombohedrally distorted perovskite. Taking these data into account, it should be noted that the morphotropic boundary in the system $\text{LaCoO}_3 - \text{LaGaO}_3$ passes near the composition with x slightly less than 0.7.

The IR absorption spectra of lanthanum cobaltite LaCoO_3 in the wave number interval $450 - 270 \text{ cm}^{-1}$ has two strong absorption bands — ν_{b-h} and ν_{b-l} , which are due to the deformation vibrations of the bridge bond $\text{Co}(\text{Ga})-\text{O}-\text{Co}(\text{Ga})$, whose frequencies are 420 and 434 cm^{-1} , respectively (see Fig. 2, curve 1). As the degree of substitution of the Ga^{3+} ions for the Co^{3+} ions increases from 0 to 0.5, the intensity of the absorption band ν_{b-h} remains high, and its frequency gradually increases; for the solid solution with $x = 0.5$ it equals 429 cm^{-1} (see Fig. 2, curve 7). As the degree of substitution increases from 0 to

0.5, a substantial decrease of the intensity and a gradual increase of the frequency of the absorption band ν_{b-l} from 343 cm^{-1} for LaCoO_3 to $\approx 370\text{ cm}^{-1}$ for the solid solution with $x = 0.5$ (see Fig. 2, curve 7) are observed. Together with a decrease of the intensity of the absorption band ν_{b-l} in the frequency range $343 - 370\text{ cm}^{-1}$, the intensity of the third absorption band near 400 cm^{-1} gradually increases, the latter band being virtually absent in LaCoO_3 . For the solid solution with $x = 0.5$ this absorption band lies near the absorption band $\nu_{b-h} = 429\text{ cm}^{-1}$ (see Fig. 2, curve 7), and its frequency is 402 cm^{-1} . As the degree of substitution increases further from 0.5 to 0.7, these two absorption bands merge into a single band, whose frequency is 400 cm^{-1} (see Fig. 2, curve 8). In addition, two more absorption bands, which are hardly noticeable, appear at frequencies ≈ 350 and 330 cm^{-1} . For the solid solution with $x = 0.95$ the frequencies of these absorption bands equal 349 and 326 cm^{-1} (see Fig. 2, curve 11).

In summary, cobaltites – gallates belonging to the binary system $(1-x)\text{LaCoO}_3 - x\text{LaGaO}_3$ ($0 \leq x \leq 1.0$) were synthesized. X-ray phase analysis showed that a continuous series of solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ forms in this system. It was determined that the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$, where no more than 70% of the Co^{3+} ions in LaCoO_3 are replaced with Ga^{3+} ions ($0 \leq x \leq 0.7$), possess the crystal structure of rhombohedrally distorted perovskite while the solid solutions containing more than 70% Ga^{3+} ions ($0.7 < x \leq 1.0$) possess the crystal structure of orthorhombically distorted perovskite. As the degree of substitution increases from 0 to 1.0 the interplanar distances of the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ gradually increase from the values for LaCoO_3 to the values for LaGaO_3 .

In the composition range of solid solutions with a rhombohedral structure ($0 \leq x \leq 0.5$) the crystal lattice parameters a and c increase from $a = 5.4428\text{ \AA}$, $c = 13.0930\text{ \AA}$ for LaCoO_3 to $a = 5.4557\text{ \AA}$, $c = 13.1567\text{ \AA}$ for $\text{LaCo}_{0.5}\text{Ga}_{0.5}\text{O}_3$.

Analysis of the IR spectra obtained for the solid solutions $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ showed that the morphotropic bound-

dary separating the region of solid solutions with rhombohedrally and orthorhombically distorted perovskite structure lies near the composition of the solid solution $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ with x slightly less than 0.7.

The data obtained can be used to develop new functional oxides of materials with a prescribed system of properties which are intended for fabricating various devices of electronic technology and so forth.

REFERENCES

1. S. F. Pal'guyev, V. K. Gil'derman, and V. I. Zemtsov, *High-Temperature Oxide Electronic Conductors for Electrochemical Devices* [in Russian], Nauka, Moscow (1990).
2. N. Bonanos, K. S. Knight, and B. Ellis, "Perovskite solid electrolytes: Structure, transport properties, and fuel cell applications," *Solid State Ionics*, **79**(1), 161 – 170 (1995).
3. T. Yu. Glavatskikh, N. U. Venskovich, V. V. Aleksandrovskii, et al., "Production and properties of oxygen-selective ceramic based on lanthanum gallate with ionic-electronic conductivity," *Neorg. Mater.*, **39**(7), 892 – 896 (2003).
4. K. Huang, R. Tichy, and J. Goodenough, "Oxide-ion conductor: Strontium- and magnesium-doped LaGaO_3 : I, Phase relationships and electrical properties," *J. Am. Ceram. Soc.*, **81**(10), 22565 – 2575 (1998).
5. V. G. Bhide, D. S. Rajoria, and Rama Rao, "Mössbauer studies of the high-spin — low-spin equilibria and the localized-collective electron transition in LaCoO_3 ," *Phys. Rev.*, **6**(3), 1021 – 1032 (1972).
6. P. G. Radaelli and S.-W. Cheong, "Structural phenomena associated with the spin-state transitions in LaCoO_3 ," *Phys. Rev. B*, **66**(6), 094408-1 – 094408-9 (2002).
7. C. Zobel, M. Kriener, D. Bruns, et al., "Evidence for a low-spin to intermediate-spin state transitions in LaCoO_3 ," *Phys. Rev. B*, **66**(3), 020402-1 – 020402-3 (2002).
8. *Powder Diffraction File*, Newton Square, ICDD (2001), No. 84-0846.
9. *Powder Diffraction File*, Newton Square, ICDD (2001), No. 24-1102.
10. *Powder Diffraction File*, Newton Square, ICDD (2001), No. 48-0123.